

High Performance Si Negative Electrode Composed of Silicate Inorganic Binder

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ABSTRACT

Use of a silicate inorganic binder was investigated with the goal of suppressing volume expansion of Si negative electrodes associated with charge-discharge.

Use of a Si negative electrode with the electrode density lowered by conductive carbon and with inorganic binder permeated to the electrode interior enabled control of the amount of electrode expansion associated with charge-discharge and suppression of delamination from the current collector and conductive path breakdown within the active material layer. This realized a high-performance Si negative electrode with a large reversible charge-discharge capacity.

XPS analysis and STEM-EDX analysis were performed to elucidate these factors. The results showed that in electrodes coated with an inorganic binder, a network of siloxane bonds formed and strong bonds were obtained, and an interface phase in which the Si and inorganic binder are fused also formed.

1. Introduction

Development and popularization of electric vehicles (EV) and fuel cell vehicles (FCV) is one solution for helping realize a low-carbon society. Further increases in battery energy density are desired for automotive application of lithium-ion batteries^{(1), (2)}, and methods that use active materials with a large capacity are being investigated as one approach. Si has a high theoretical capacity of 4200 mAh/g, which makes it attractive as an active material for the negative electrodes of next-generation lithium secondary batteries, but volume changes associated with the charge-discharge reaction are large and lead to electrode disintegration. Therefore, it is important to achieve an electrode design that maintains the electrode structure⁽³⁾⁻⁽¹⁰⁾.

The binder types, conductive carbon type, electrode composition, and other factors are being investigated with the goal of maintaining the electrode structure of Si electrodes⁽³⁾⁻⁽⁵⁾. As shown in Fig. 1, binders can be broadly classified into “organic binders” and “inorganic binders”⁽⁶⁾⁻⁽⁸⁾. However, this research focused on a silicate inorganic binder

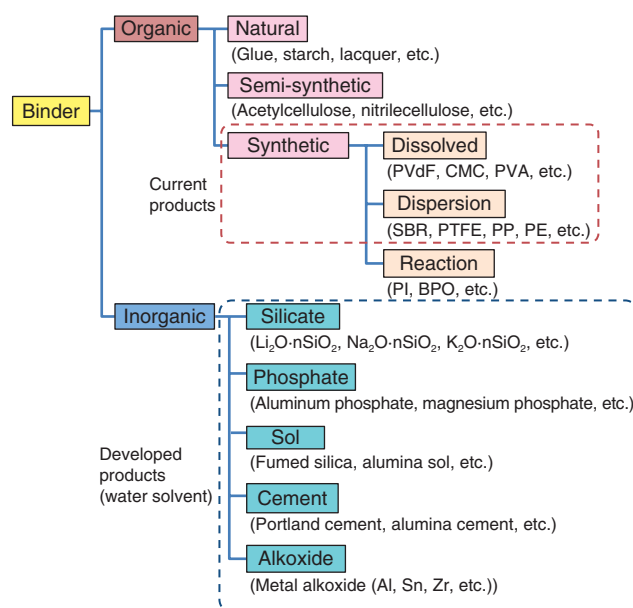


Fig. 1 Classification of binders

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(hereafter, inorganic binder), which has strong binding force for maintaining the electrode structure⁽¹¹⁾.

It has been demonstrated that when an inorganic binder $A_2O \cdot nSiO_2$ ("A" indicates an alkali metal) undergoes hydrolysis, a silanol (-Si-OH) group is generated and adsorbed to the inorganic material surface by hydrogen bonding, and when this is heated a dehydration condensation reaction occurs, enabling the formation of a strong siloxane (-Si-O-Si-) bond^{(12), (13)}.

It is anticipated that when Si is used as the active material, the active material surface is etched under the condition of an alkaline aqueous solution ($pH \leq 11$), and the -Si-OH group is formed on the Si surface by the reaction shown in Eq. (1)^{(14), (15)}.



When this Si surface etching reaction occurs, the Si of the inorganic binder and the Si of the active material integrate as shown in Fig. 2, and a powerful binding action can be expected, especially when Si active material is used. However, there are no known reports that describe the detailed interface structure.

This research attempted to use an inorganic binder to obtain a high-performance Si negative electrode with enhanced reversible charge-discharge capacity. At the same time, an attempt was also made to evaluate the binding force of the inorganic binder and to clarify the bonding scheme of the inorganic binder and the interface structure between the Si active material and the inorganic binder, which are factors enhancing the binding force.

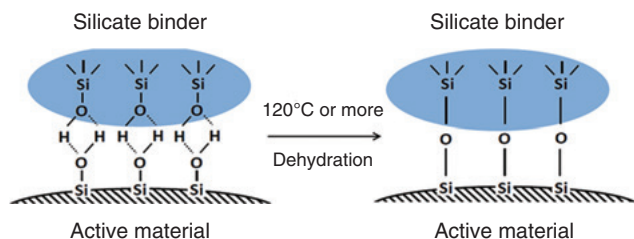


Fig. 2 Reaction mechanism of silicate inorganic binder

2. Experimental Method

2.1. Si Negative Electrode Sample Prototypes

As inorganic binders are higher density compared with conventional organic binders⁽⁸⁾, a higher mass ratio is needed to obtain sufficient binding force by the slurry coating method. Therefore, methods are being investigated for applying inorganic binder aqueous solution as a structure forming agent by permeating it into a conventional electrode and then heat-treating the electrode as shown in Fig. 3⁽⁶⁾⁻⁽¹⁰⁾. In this process, the electrode structure is the key to uniformly permeating the inorganic binder into the electrode, and porosity adjustment is needed to enable the

Table 1 List of electrode samples

No.	Conductive carbon		Silicate binder
1	AB1	5 wt%	None
2			$K_2O \cdot 3SiO_2$
3	AB2	20 wt%	$K_2O \cdot 3SiO_2$
4		20 wt%	$K_2O \cdot 3SiO_2$

inorganic binder to permeate.

Conductive carbon forms conductive paths and also plays a role to retain the electrolyte solution in the pores. For example, it has been demonstrated that the more developed the chain structure (structure) of acetylene black (AB), the higher the conductivity and fluid retentivity⁽¹⁶⁾. This research investigated AB conductive carbon with different structures in order to enhance the permeability and conductivity of the inorganic binder.

Electrodes of the levels shown in Table 1 were fabricated using the conductive carbons AB1 and AB2 with the physical properties shown in Fig. 4. Compared to AB1, AB2 has a smaller particle size and a more developed structure, and thus it is thought to better enhance the impregnating ability of the inorganic binder and create conductive paths⁽¹⁶⁾. In addition, increasing the conductive

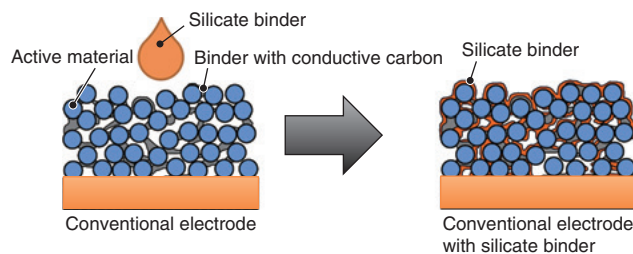


Fig. 3 Manufacturing process of Si electrode

Item	AB1	AB2
Particle size (nm)	37	23
Specific surface area (m ² /g)	58	133
Quantity of iodine adsorption (mg/g)	82	180
Packing density (g/ml)	0.08	0.05
Image of AB structure		

Fig. 4 Physical property values of conductive carbons

carbon quantity can also be expected to enhance the impregnating ability and conductive paths.

Each conductive carbon was used to prepare slurries containing 4 wt% styrene butadiene rubber (SBR) as a binder and 1 wt% sodium carboxymethyl cellulose (CMC) as a thickener. The prepared slurries were then applied to current collectors (copper foil) and allowed to dry to obtain precursors of each negative electrode. The precursor coating amount was adjusted to approximately 2.3 mg/cm². An inorganic binder aqueous solution (K₂O·3SiO₂ 10 wt%) was applied by the spray method to the obtained negative electrode precursors of samples No. 2 to No. 4, allowed to permeate, and then heat-treated using a 120°C drying furnace to cure the inorganic binder and obtain negative electrodes for use as test electrodes.

2.2. Evaluation of Samples

2.2.1. Measurement of electrode DC resistance

The composite layer DC resistance of the electrode sheet of each prepared negative electrode was measured using the Electrode Resistance Measurement System RM2610 (HIOKI E.E. Corporation).

2.2.2. Observation of electrode cross-section and distribution of inorganic binder

Cross-section magnified observation of negative electrode samples No. 2 to No. 4, which were coated with inorganic binder, was performed using a scanning electron microscope (SEM). In addition, an electronic probe micro analyzer (EPMA) was used to map the potassium (K) element, which is a component derived from the inorganic binder, and the distribution of inorganic binder permeation in the cross-section was examined. The observation samples were made by punching a ϕ 5-mm-size piece from each negative electrode, cutting to halve the electrode area, and then cross-section polishing the obtained cut surface by Ar ion milling.

2.2.3. Evaluation of binding force of binder

The shear strength was evaluated using the Surface and Interfacial Cutting Analysis System (SAICAS) in order to evaluate the electrode internal binding force of negative electrodes No. 1 and No. 2. The measurement conditions were a Borazon blade (blade width 1.0 mm), rake angle 20°, clearance angle 10°, horizontal speed 2 μ m/s, and vertical speed 0.2 μ m/s. The blade was moved horizontally at the three depth points of 5 μ m, 10 μ m, and 15 μ m, and the shear strength was obtained by Eq. (2).

$$\tau = \frac{F_h}{2wd \cot \phi} \quad (2)$$

τ : Shear strength

F_h : Horizontal load

w : Blade width

d : Shear thickness

ϕ : Shear angle

The deemed shear strength assumes $\phi = 45^\circ$.

2.2.4. Analysis of Si-O bonding in electrodes

The electrodes coated with inorganic binder were analyzed by X-ray photoelectron spectroscopy (XPS) to confirm whether Si-O bonds were newly formed due to the inorganic binder. XPS measurement was performed of negative electrodes No. 1 and No. 2, and the spectrum near Si 2p was compared. The Si-O bonding ratio was calculated from the spectral area ratio.

2.2.5. Analysis of interface between active material and inorganic binder

A scanning transmission electron microscope (STEM) was used to analyze the inorganic binder coating state and the composition of the interface between the active material and the inorganic binder of negative electrode No. 2, which was coated with inorganic binder. STEM observation was performed for an approximately 300-nm-square area, and the presence and thickness of the interface phase was investigated. In addition, element analysis was performed by energy dispersive X-ray spectroscopy (EDX), and the respective ratios of alkali metal atoms to all constituent atoms (at%) in the active material, interface phase and inorganic binder phase were estimated from the EDX spectral intensity. Element mapping measurement was also performed by EDX.

2.3. Evaluation of Cells

2.3.1. Coin cell prototypes

Coin cells (R2032) were fabricated using a negative electrode (ϕ 14 mm) as the test electrode, lithium metal foil (ϕ 16 mm) as the counter electrode, nonwoven glass fabric (Advantec GA100) as the separator, and an electrolyte consisting of lithium hexafluorophosphate (LiPF₆) dissolved in ethylene carbonate (EC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) (1.1 M LiPF₆/EC:EMC:DEC = 3:4:3 vol.).

2.3.2. Evaluation of coin cells

The capacity of each negative electrode during the first charge-discharge cycle was confirmed with a test environment temperature of 25°C, current density of 0.025 C-rate, and cutoff potential varied from 0.01 V to 1.5 V (potential versus Li⁺/Li).

2.3.3. Observation of electrode cross-section after charge-discharge

The coin cells were disassembled after the first charge-discharge cycle, and cross-section SEM observation was performed of negative electrodes No. 1 and No. 2.

3. Results and Examination

3.1. Degree of Inorganic Binder Permeation due to Conductive Carbon

3.1.1. Electrode density and inorganic binder quantity

Table 2 shows the inorganic binder mass ratio, the

Table 2 Electrode density and silicate binder ratio

No.	Conductive carbon		Silicate binder ratio (wt%)	Electrode density (g/cm ³)	
				Precursor	With silicate binder
1	AB1	5 wt%	-	0.83	-
2			11		0.87
3		20 wt%	10.2	0.98	0.87
4	AB2	20 wt%	20	0.66	0.7

precursor electrode density, and the electrode density after coating with inorganic binder for each negative electrode sample. In the electrodes that used AB1, the electrode density before coating with inorganic binder increased together with the conductive carbon quantity. However, the conductive carbon quantity did not produce a large change in the inorganic binder ratio. In the electrode that used AB2, which has a small particle size and a developed chain structure, the electrode density dropped greatly at a conductive carbon quantity of 20 wt%, and the inorganic binder coating amount also increased compared to AB1. These results are thought to indicate that use of a large quantity of conductive carbon with a small particle size and a developed chain structure lowers the electrode density, which increases the porosity within the electrode, with the result that a sufficient quantity of inorganic binder aqueous solution can impregnate the electrode.

3.1.2. Composite layer DC resistance of samples

Figure 5 shows the DC resistance values of the electrode composite layer of each negative electrode. Comparison of No. 1 without inorganic binder and No. 2 with inorganic binder shows a slight increase in resistance due to coating with inorganic binder. Comparison of No. 2 (5 wt% conductive carbon quantity) and No. 3 (20 wt% conductive carbon quantity) shows that increasing the conductive carbon quantity lowered

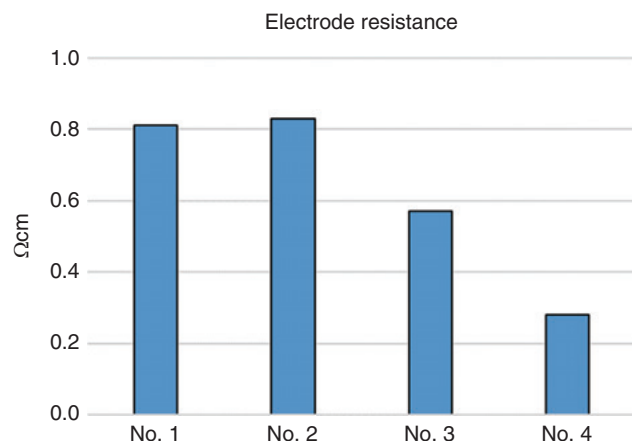


Fig. 5 Electrode DC resistance of samples

the resistance. It is thought that increasing the conductive carbon quantity enhanced the electron conductivity within the electrode. Comparison of No. 3 (AB1) and No. 4 (AB2), which use the same quantity of different conductive carbon types, shows that the resistance value dropped even further in No. 4 (AB2). This indicates that AB2, which has a small particle size and a developed structure, exhibits a greater conductive performance enhancement effect.

3.1.3. Observation of sample cross-section and distribution of inorganic binder

Figure 6 shows cross-section SEM images and EPMA mappings of K element, which is a component derived from the inorganic binder, for negative electrode samples No. 2 to No. 4. In samples No. 2 and No. 4, which had a low negative electrode precursor density, the K element derived from the inorganic binder was confirmed to sufficiently permeate to the current collector interface of the entire negative electrode layer. In contrast, the K element was unevenly distributed near the surface of the negative electrode layer in sample No. 3, which had a high negative electrode precursor density.

It is thought that the low electrode density of the negative electrode precursor enabled porosity to form inside the negative electrode precursor, so a sufficient quantity of inorganic binder aqueous solution could impregnate from the electrode interior to the current collector interface. In the high-density sample No. 3, however, it is thought that sufficient porosity was not obtained, and thus the inorganic binder could not permeate to the electrode interior.

3.2. Charge-discharge Performance Enhancement Effect of Inorganic Binder

3.2.1. Evaluation of coin cells

The capacity of coin cells using negative electrode samples No. 1 to No. 4 was measured. Figure 7 shows the respective first charge-discharge curves, and Table 3 shows the respective first charge-discharge capacities and efficiency.

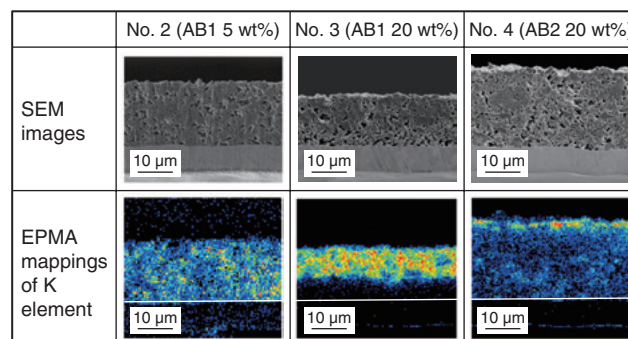


Fig. 6 Cross-section SEM images and EPMA mappings of K element

Table 3 First charge-discharge capacity and efficiency

No.	Capacity (mAh/g)		Efficiency (%)
	Charge	Discharge	
1	2346	397	16.3
2	3059	2550	83.4
3	3657	695	19.0
4	4164	3885	93.3

Coating with inorganic binder greatly increased the first reversible capacity from 397 mAh/g to 2550 mAh/g. Sample No. 4, which used large quantities of conductive carbon and inorganic binder and had the inorganic binder permeate to the electrode interior, exhibited a first charge capacity of 4164 mAh/g, which is close to the theoretical capacity of Si, and the high reversibility of a first charge-discharge efficiency of 93.3%. The enhanced discharge characteristics of sample No. 4 are thought to be the effect of the inorganic binder and also the enhancement of electron conductivity within the electrode. In contrast, sample No. 3 used a large quantity of conductive carbon, but the inorganic binder was unevenly distributed only near the surface, so although first charge could be adequately performed, the charge-discharge efficiency was just 19% and the inorganic binder had little effect. This showed that it is important for the inorganic

binder to permeate sufficiently to the electrode interior in order to manifest adequate effects.

3.2.2. SEM observation of cross-section after charge-discharge

Figure 8 shows cross-section SEM images of electrodes No. 1 and No. 2 after the first charge-discharge cycle in coin cell evaluation. Large volume expansion of the electrode composite layer and delamination around the current collector were confirmed in the electrode not coated with inorganic binder. It is thought that delamination occurred during first charge, with the result that conductive paths broke down and discharge was impaired. In the Si electrode coated with inorganic binder, some cracking occurred within the electrode, but volume expansion was

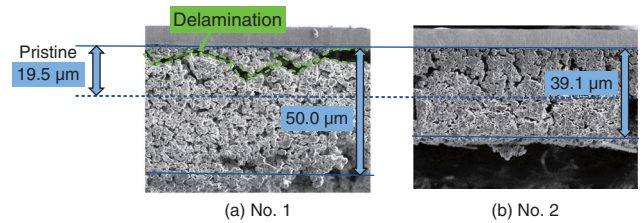


Fig. 8 Cross-section SEM images after first cycle

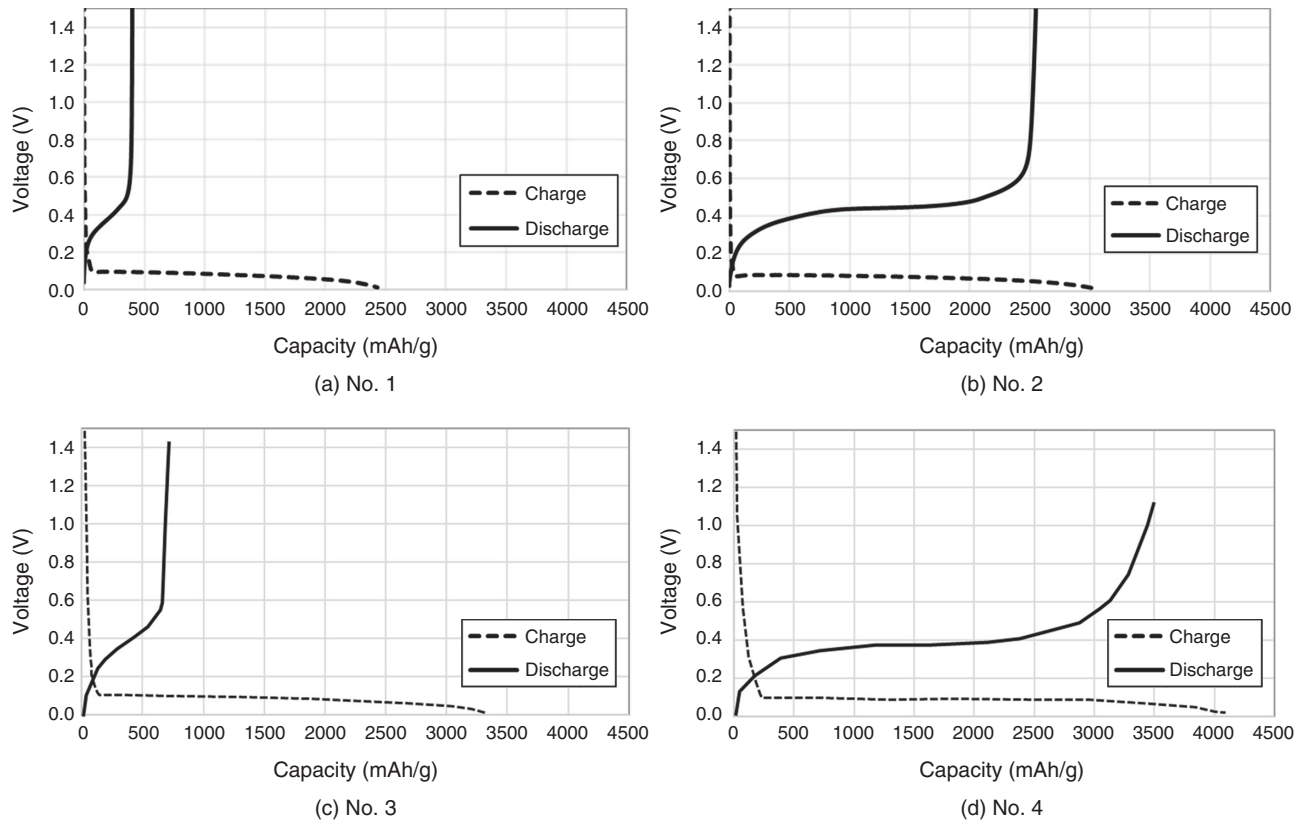


Fig. 7 First charge-discharge curves of Si/Li coin cells at 0.025 C

suppressed and delamination from the current collector was not confirmed. These results are thought to indicate that the bond between the active material and the inorganic binder increased the binding force of the electrode, which led to increased reversible capacity.

3.3. Analysis of Binding Action of Inorganic Binder

3.3.1. Evaluation of bonding force inside electrodes using SAICAS

Figure 9 shows SAICAS measurements of the shear strength τ inside electrodes No. 1 and No. 2. The inorganic binder coating increased the shear strength, which indicates the binding force inside the electrode, by around four times. This shows that coating with inorganic binder forms strong bonds inside the electrode composite. The strength tended to decrease as the depth increased, which is thought to be an impact of the SBR binder distribution prior to coating with inorganic binder. The slope of this tendency is roughly the same regardless of the presence of inorganic binder, which infers that the inorganic binder was uniformly distributed to the electrode interior and increased the strength.

3.3.2. XPS analysis of Si-O bonding

Figure 10 shows the Si 2p spectra of electrodes No. 1 and No. 2 obtained by XPS measurement. A peak around 99 eV that indicates Si-Si bonding and a peak around 103 eV that indicates Si-O bonding were confirmed in each sample. Table 4 shows the detected Si-O bonding ratio of all Si. Coating with inorganic binder was confirmed to increase the Si-O bonding ratio of all Si. This means that in addition to the SiO_2 originally present near the Si active material surface, silicate-derived Si-O bonding is also thought to increase in electrodes coated with inorganic binder.

Furthermore, the Si-O bonding peak shifted to the lower energy side in electrodes coated with inorganic binder. The

Table 4 Si-O bonding ratio for all Si

Sample	Si-O bonding ratio (%)
No. 1 precursor	32
No. 2 with silicate binder	48

bonding energy of SiO_2 is 103.2 eV to 103.9 eV, but the bonding energy of silicate is 102 eV to 103 eV, and thus it can be inferred that this peak shift occurred due to the increase in Si-O bonds derived from the inorganic binder. These results suggest that a network of strong Si-O bonds deriving from the inorganic binder formed in the electrodes coated with inorganic binder.

3.3.3. Analysis of interface between active material and inorganic binder

Figure 11 shows the EDX mapping of an 18- μm -square area of sample No. 2. Here, O and K elements, which are inorganic binder components, were observed around the Si

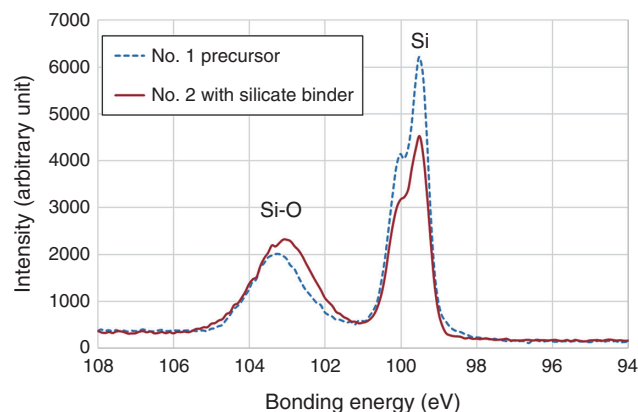


Fig. 10 XPS spectra of Si 2p peak of Si electrode

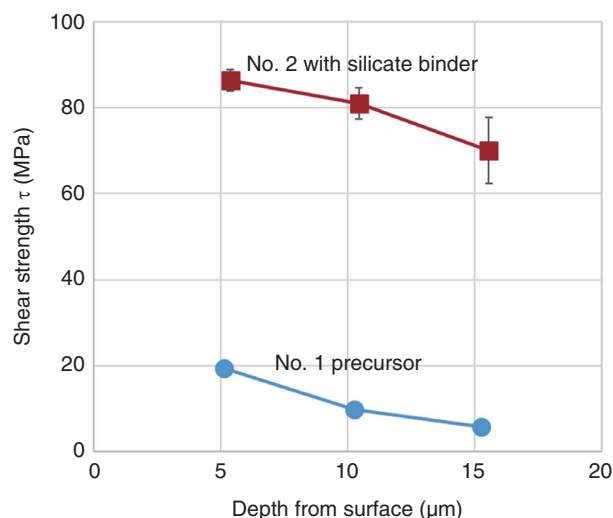


Fig. 9 Shear strength in electrode

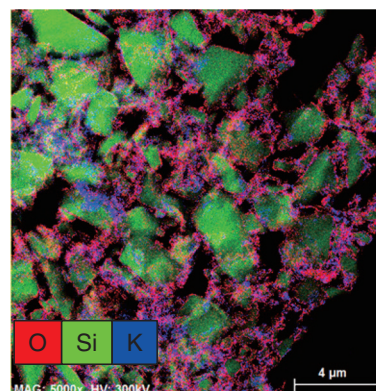


Fig. 11 EDX mapping (18 μm $\times$ 18 μm) of electrode No. 2

active material.

Figure 12(a) shows a STEM image of the Si active material surface. An inorganic binder phase with a thickness of approximately 40 nm was confirmed on the Si active material surface. Figure 12(c) shows the EDX line analysis results of the Si, O, and K elements in the interface domain between the Si active material and the inorganic binder in the direction of the arrow in Fig. 12(b). Table 5 shows the respective element ratio in each of active material phase A, interface phase B, and inorganic binder phase C, as shown in Fig. 12(c). Figure 13 shows an image drawing of the element distribution of the interface phase. Interface phase B was found to have a greater K element content compared with the inorganic binder phase C. The reason for this is thought to be that the Si of the active material and the inorganic binder reacted as per Eq. (1), and neutralization of the inorganic binder progressed simultaneously with etching of the Si surface, so a large quantity of alkali metal was precipitated to the interface phase (active material surface) as a salt. In other words, it can be inferred that when the Si surface of the active material is dissolved by etching, -Si-O-Si- bonds form that have strong bonding force and integrate with the inorganic binder, which forms an even stronger interface.

Table 5 Element ratio of interface domain

	Phase A Si grain	Phase B Interface	Phase C Silicate binder
Si (at%)	93.8	43.9	37.8
O (at%)	6	54.4	62.1
K (at%)	0.2	1.7	0.1

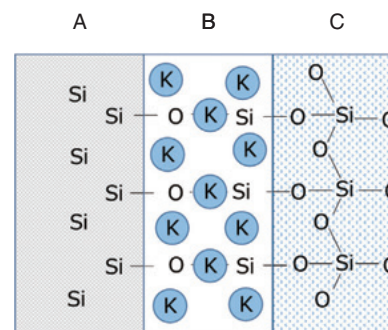


Fig. 13 Element distribution model of interface domain

4. Conclusion

A silicate inorganic binder was applied to Si negative electrodes adjusted by conductive carbon. Permeation of the inorganic binder to the electrode interior enabled control of the amount of volume expansion associated with charge-discharge and suppression of delamination from the current collector, which realized a high-performance Si negative electrode with a large reversible charge-discharge capacity. The factors for this were analyzed, and the following conclusions were reached.

Coating with inorganic binder increased the bonding force inside the electrode to around four times that of an uncoated electrode. XPS analysis showed that Si-O bonds formed inside the electrode due to the inorganic binder.

Composition analysis of the interface between the active material and the inorganic binder revealed the presence of an interface phase with large quantities of alkali metal elements. This interface phase supports the hypothesis that the Si surface is etched by the alkaline aqueous solution and the Si and inorganic binder integrate.

It was clarified that in addition to -Si-O-Si- bonding between inorganic binders, the formation of an interface phase in which the Si and inorganic binder are fused is key to realizing a high-performance Si negative electrode that can maintain an electrode framework capable of withstanding the expansion and contraction of Si.

References

- (1) NEDO: Jisedai jidosha no bunya niokeru sumato komyunitei infura to hyojunka no arikata ni kakaru

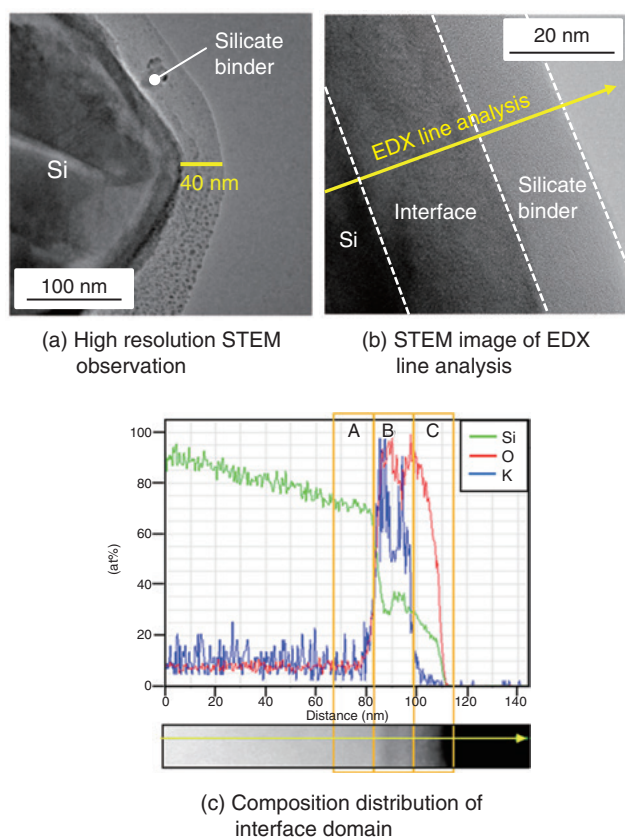


Fig. 12 STEM image and EDX line analysis of Si surface

- kento, (2016) (in Japanese)
- (2) NEDO: EV PHV rodō mappu kentokai hokokusho, (2016) (in Japanese)
 - (3) Mukai, T., Yamashita, N., Ikeuchi, Y., Sakamoto, T., Sirikon kei fukyoku no juhoden tokusei no kojo to bocho taisaku - Keisan kei mukibainda o mochiita Si fukyoku no denkyoku tokusei, Material stage, Vol. 17, No. 5, p. 29-33, (2017) (in Japanese)
 - (4) Liu, W.-R., Guo, Z.-Z., Young, W.-S., Shieh, D.-T., Wu, H.-C., Yang, M.-H., Wu, N.-L.: Effect of electrode structure on performance of Si anode in Li-ion batteries: Si particle size and conductive additive, Journal of Power Sources, Vol. 140, Issue 1, p. 139-144, (2005)
 - (5) Qiao, H.-B., Tian, X.-M., Yi, T.-F.: Electrochemical Properties of Si Negative Electrodes Bonded with Partially Hydrolyzed Polyacrylamide for Li-ion Batteries, International Journal of Electrochemical Science, Vol. 8, Issue 7, p. 9414-9420, (2013)
 - (6) Li, J.-T., Wu, Z.-Y., Lu, Y.-Q., Zhou, Y., Huang, Q.-S., Huang, L., Sun, S.-G.: Water Soluble Binder, an Electrochemical Performance Booster for Electrode Materials with High Energy Density, Advanced Energy Materials, Vol. 7, Issue 24, 1701185, (2017)
 - (7) Mukai, T., Ikeuchi, Y., Sakamoto, T., Yamashita, N., Kinoshita, T., Takahashi, M., Tanaami, K., Aoyagi, S.: Dai II hen Dai 2 sho Sirikon fukyokuyo mukikeisankei bainda, Recent Developments of Silicon Anodes for Lithium Ion Batteries, CMC Publishing Co., Ltd., p. 164-170, (2019) (in Japanese)
 - (8) Mukai, T., Ikeuchi, Y., Sakamoto, T., Yamashita, N.: Dai 3 sho Fukyoku zairyo no kaihatsu, Posuto richiumu ni muketa kakushinteki niji denchi no zairyo kaihatsu, NTS Inc., p. 145, (2018) (in Japanese)
 - (9) Mukai, T., Yanagida, M., Sakamoto, T.: Dai 4 sho Dai 2 setsu Richiumu ion niji denchi no tokusei kojo ni muketa funtai gijutsu, Richiumu ion niji denchi - koyoryoka tokusei kaizen ni muketa buzai sekkei apurochi to hyoka shuho -, Johokiko Co., Ltd., p. 210-219, (2017) (in Japanese)
 - (10) Iwanari, D., Yoshida, K., Tanaka, K., Ikeuchi, Y., Sakamoto, T., Yamashita, N., Mukai, T.: Dai 7 sho Dai 4 setsu Sirikon funmatsu no seizohoho to keisankei mukibainda o mochiita DG-Si fukyoku no denkyoku tokusei, Jisedai denchi yo denkyoku zairyo no koenerugi mitsudo koshutsuryokuka, TECHNICAL INFORMATION INSTITUTE CO., LTD., p. 145, (2017) (in Japanese)
 - (11) Fuchs, J. N.: Ueber ein neues Product aus Kieselerde und Kali; und dessen nützliche Anwendung als Schuzmittel gegen schnelle Verbreitung des Feuers in Theatern, als Bindemittel, zu firnißartigen Anstrichen u.s.w., Polytechnischen Journals, 17, CIV, p. 465-481, (1825)
 - (12) Arkles, B., Steinmetz, J. R., Zazyczny, J., Mehta, P.: Factors contributing to the stability of alkoxysilanes in aqueous solution, Silanes and Other Coupling Agents, p. 91-104, (1992)
 - (13) Fukushima, T.: Mechanisms of Hardening and Deterioration of Films of Water Glass Inorganic Binders, Materials Life, Vol. 6, No. 3, p. 146-157, (1994) (in Japanese)
 - (14) Sotoaka, R.: New Etchants for High Speed Anisotropic Etching of Silicon, Journal of the Surface Finishing Society of Japan, Vol. 59, No. 2, p. 104-106, (2008) (in Japanese)
 - (15) Morinaga, H.: Cleaning technology for new materials, Oyo Buturi, Vol. 70, No. 9, p. 1067-1073, (2001) (in Japanese)
 - (16) Nagai, T.: Dai 3 sho Dai 7 setsu Koenerugi mitsudoka ni muketa dodenzai no bunsansei kojo gijutsu, Richiumu ion niji denchi - koyoryoka tokusei kaizen ni muketa buzai sekkei apurochi to hyoka shuho -, Johokiko Co., Ltd., p. 166-181, (2017) (in Japanese)

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